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(54) **Lubricating compositions**

(57) Oil-soluble dispersant useful as luboil additive which comprises a polyolefin substituted dicarboxylic acid or anhydride, in which the number average molecular weight (Mn) of the polyolefin is from 1500 to 5000 and the molar equivalent ratio (as hereinbefore defined) of dicarboxylic acid groups to equivalent of polyolefin substituent is less than 1.3. The polyolefin substituted dicarboxylic acid or anhydride can be further reacted with amines or alcohols to form other useful dispersant additives.

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LUBRICATING COMPOSITIONS

The present invention relates to oil-soluble dispersants, useful as additives for luboils, based on polyolefin-substituted dicarboxylic acid derivatives.

US Patent No. 4234435 discloses as oil additives polyolefin substituted dicarboxylic acid derivatives based on polyolefins having a molecular weight (Mn) of 1300 to 5000 and containing within their structure at least 1.3 succinic groups for each equivalent weight of polyolefin. These products have become established as dispersant additives for lubricating oils, being of the dispersant type often referred to as "ashless" because of the absence of a metal component.

European Patent Application 0208560 discloses similar products formed by reacting a polyolefin (suitably polyisobutylene; PIB) with maleic anhydride, leading to an adduct containing 1.05 to 1.25 maleic moieties per molecule of polyolefin originally present in the reaction mixture. It will be readily apparent to those skilled in the art that complete reaction of all the polyolefin (e.g. PIB) with the maleic anhydride (MALA) is unattainable in practice, in which case the MALA/PIB ratio in the actual chemical adduct formed will be higher than

would be calculated on the basis of total polyolefin originally present in the reaction mixture. Thus, when 80% of the polyolefin is taken up into the product (representing an operationally realistic result) a MALA/PIB ratio of 1.05 to 1.25 based on total polyolefin reactant originally present (i.e. as defined in EPA 0208560) effectively becomes a product molecular ratio of about 1.3 to 1.5, i.e. similar to those of USP 4234435.

Applicants have found that polyolefin-succinic type products in which the actual ratio of succinic groups to polyolefin chains is below 1.3 show particularly useful properties, including a reduced level of interaction with other additives normally present in lubricating oil packages, and moreover give good results in the more severe engine test VE. Accordingly, the present invention provides an oil soluble dispersant useful as a luboil additive which comprises a polyolefin-substituted dicarboxylic acid or anhydride, in which the number average molecular weight (Mn) of the polyolefin is from 1500 to 5000 and the molar equivalent ratio of dicarboxylic acid producing groups to polyolefin groups is less than 1.3, preferably between 1.0 and 1.2.

As is apparent from the patent specifications quoted above, the dicarboxylic acid/polyolefin ratio can be calculated and expressed in different ways, and for the avoidance of any doubt it should be clearly understood that for the purposes of the present invention the "molar equivalent ratio" is the molar ratio in the actual product of dicarboxylic acid (or anhydride) groupings to equivalents of polyolefin substituent. The molar equivalent ratio can be easily calculated by the following expression:

$$r = \frac{Mn \times AV}{(20xAM - AVx96)}$$

in which:

M_n = Number average molecular weight of the PIB
AV = Acid value of the reaction product (mmol/g)
AM = Active matter in the reaction product (%m)
"Active matter" denotes polyolefins bearing carboxylic acid groupings, from which it will be understood that the unreacted nonpolar polyolefins do not contribute to the AM.

The polyolefin-substituted carboxylic acid/derivative is preferably derived by reacting an alpha-beta unsaturated carboxylic acid or active derivative thereof with a polyolefin, suitably a homopolymer or copolymer of one or more olefin monomers having 2 to 16, preferably from 2 to 6, carbon atoms. The copolymers include random, block and tapered copolymers. Suitable monomers include ethene, propene, butenes, isobutene, pentenes, octenes, and also diolefines such as butadiene and isoprene. If a diene is used as monomer the resulting polymer is preferably hydrogenated to saturate at least 90%, more preferably substantially all unsaturated bonds. It is especially preferred to use a polyolefin substituent derived from polyisobutylene.

The number average molecular weight of the polyolefin substituent is suitably not greater than 5000, since molecular weights above 5000 can give handling problems in the reaction due to the viscosity levels. To reduce the risk of problems the number average molecular weight is preferably below 3000 but above 1800 since low molecular weight products tend to be less effective as dispersants.

The number average molecular weight (Mn) can easily be determined by vapour pressure osmometry or by gel permeation chromatography with calibration of the polymer, as will be appreciated by those skilled in the art. The weight average molecular weight (Mw) can also be determined by gel permeation chromatography. The quotient Mw/Mn, which is a measure indicating the width of molecular weight distribution, suitably has a value from 1.5 to 4.0.

The dicarboxylic acid is suitably derived from an alpha-beta unsaturated dicarboxylic acid, anhydride or ester, such as maleic, fumaric, itaconic, etc.; maleic acid (anhydride) being particularly preferred, in which case the dicarboxylic acid grouping in the present product is thus a succinic acid derivative.

The polyolefin-substituted carboxylic acids may be prepared according to established procedures from an alkene of required molecular weight and an appropriate amount of the unsaturated dicarboxylic acid or active derivative. Thus, the polyolefin, e.g. polyisobutylene, may be contacted with maleic acid or anhydride at a temperature of 140 to 220°C, optionally in the presence of chlorine, e.g. as described in e.g. UK Patent 949,981. The proportions of polyolefin and maleic anhydride and also chlorine, when used, are selected so as to yield the desired MALA/polyolefin ratio in the final product. Another method for the preparation of polyolefin substituted succinic anhydride is described in USP-3, 172, 892, according to which a halogenated, in particular chlorinated, polyolefin is reacted with maleic anhydride.

From e.g. NL-A-74 12 057 it is known to prepare hydrocarbon-substituted succinic anhydride by

thermally reacting a polyolefin with maleic anhydride, a procedure which may be combined with that of UK 949,981, as is illustrated in UK 1,440,219 and UK 1,543,627. The products prepared in this way include compounds in which the polyolefin chain is connected to the alpha and/or the beta carbon atoms of the succinic group.

This acid or anhydride material is useful per se as an additive, e.g. a dispersant additive, for example in the same manner as previously known polyolefin substituted dicarboxylic acid or anhydride acylating agents disclosed in the U.S. Patent 3,288.714 where prior acylating agents are used as dispersant/detergents and U.S. 3,714,042 where prior acylating agents are used to treat overbased metal complexes. Also, the material of the invention can be used in the manner described in U.S. 3,714,017 wherein overbased detergents are treated with acylating agents.

The polyolefin dicarboxylic acid product of the invention can also be further reacted with amines, alcohols, including polyols, amino-alchols, polyoxyalkylene polyamines, hydroxyamines (as described, for example, in EPA 0208560), and mixtures thereof to form other useful dispersant additives. Particularly effective dispersant materials are obtained by reacting the polyolefin-dicarboxylic acid (anhydride) with a C_{6-50} amine containing 4 to 10 nitrogen atoms and/or an alkane polyol having at least two hydroxy groups.

The amines employed in the instant invention can be branched or unbranched, saturated, aliphatic, primary or secondary amines and are preferably higher polyamines such as alkylene polyamines, wherein pairs

of nitrogen atoms are joined by alkylene groups of 2 to 4 carbon atoms. Thus, polyamines of the formula:

$$NH_2(CH_2)_n\text{-------}[NH(CH_2)_n]_m\text{--------}NH_2$$

are included where n is 2 to 4 and m is 2 to 8. In some instances the value of n may vary at different parts of the molecule. Examples of such polyamines include triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, and higher ethylene polyamines, tripropylene tetramine, triethylene N-aminoalkyl piperazines, e.g., N-(2-aminoethyl) piperazine, N,N'-di(2-aminoethyl) piperazine, etc. Preferred are tetraethylene pentamine, pentaethylene hexamine. Commercial sources of these products, which are generally used for operational convenience, normally contain mixture of different polyamines, with one or more products predominating.

The alkane polyols useful in making the esters are alkane polyols having at least two and preferably at least four hydroxy groups such as the trihydroxyalkanes, e.g. ethylene glycol, propylene glycol, polymethylene glycols, trihydroxybutanes, pentanes, hexanes, heptanes, octanes, nonanes, dodecanes, etc., as well as tetrahydroxy alkanes, pentahydroxy alkanes, hexahydroxy alkanes, and the sugar alcohols such as erythritol, pentaerythritol, tetritols, pentitols, hexitols, mannitol, sorbitol, glucose and the like. Particularly preferred alcohols are pentaerythritol, dipentaerythritol and mannitol. Especially preferred is pentaerythritol.

The molar ratio of dicarboxylic compound to amine is typically between about 1:1 to 4:1, preferably between about 1,5:1 and 3:1, most

preferably about 2:1 to 2.5:1. When a polyol is used, the molar ratio of alcohol to dicarboxylic compound is typically 0.6:1 to 1.3:1, preferably 0.8:1 to 1.1:1. The conditions during imide formation or esterification are typically about 150°C to 250°C for between about 1 hours and 10 hours, followed by nitrogen stripping at a similar temperature for about 1-5 hours and it is preferred that the reactions take place in the absence of oxygen. A nitrogen blanket is often used to accomplish this result.

It is also possible to subject the polyolefin-substituted carboxylic acid imides and esters to post-treatments. The invention therefore further provides an additive obtained by post-treating a polyolefin-substituted carboxylic acid imide or amide as described above, which post-treating has been carried out by an agent selected from boron oxide, boron oxide hydrate, boron halides, boron acids, esters of boron acids, carbon disulfide, H_2S, sulfur, sulfur chlorides, alkenyl cyanides, carboxylic acid acylating agents, aldehydes, ketones, urea, thiourea, guanidine, dicyanodiamide, hydrocarbyl phosphates, hydrocarbyl phosphites, hydrocarbyl thiophosphates, hydrocarbyl thiophosphites, phosphorus sulfides, phosphorus oxides, phosphoric acid, hydrocarbyl thiocyanates, hydrocarbyl isocyanages, hydrocarbyl isothiocyanates, epoxides, episulfides, formaldehyde or formaldehyde-producing compounds plus phenols, and sulfur plus phenols. These post-treatments are well-known in the art.

The polyolefin-dicarboxylic acid products of this invention and their derivatives find their prime application as additives for lubricating oils, and accordingly a further aspect of this invention is a

lubricating composition which comprises a major proportion of a lubricating oil and a minor proportion, preferably from 0.1 to 10%w, especially 0.5 to 5%w, (based on the total composition) of a polyolefin-substituted dicarboxylic derivative as defined above. The lubricating oil used in such compositions can be natural, mineral or synthetic in origin. Natural lubricating oils include animal and vegetable oils, such as castor oil. Mineral oils comprise the lubricating oil fractions derived from crude oils, coal or shale, which fractions may have been subjected to certain treatments such as clay-acid, solvent- or hydrogenation treatments. Synthetic lubricating oils include synthetic polymers of hydrocarbons, modified alkylene oxide polymers, and ester lubricants, which are known in the art. These lubricating oils are preferably crankcase lubricating oils for spark-ignition and compression-ignition engines, but include also hydraulic lubricants, metal-working fluids, automatic transmission fluids and the like. The lubricating composition may contain various other additives, known in the art, such as viscosity index improvers, e.g. linear or star-shaped polymers of a diene such as isoprene or butadiene, or a copolymer of such a diene with optionally substituted styrene. These copolymers are suitably block copolymers and are preferably hydrogenated to such an extent as to saturate most of the olefinic unsaturation. Other suitable additives include dispersant V.I. improvers such as those based on block copolymers, polymethacrylates, and the like, extreme pressure/anti-wear additives such as zinc or sodium dithiophosphates, anti-oxidants, friction modifiers or metal-containing detergents such as phenates,

sulphonates, alkylsalicylates or naphthenates, all of which detergents may be overbased.

The lubricating composition according to the invention has excellent dispersancy properties.

The lubricating composition according to the present invention is suitably prepared by blending an additives concentrate into the lubricating base oil. Such a concentrate generally comprises a lubricating oil as solvent/diluent and one or more additives in a concentrated form. Hence the present invention further provides a lubricating oil concentrate comprising a lubricating oil and a polyolefin-substituted succinimide as described above, optionally after a post-treatment as indicated supra, in an amount of 10 to 80% w based on the total concentrate.

The invention is illustrated in the following Example.

EXAMPLE

A) Preparation of polyolefin-substituted succinic anhydride

A mixture of 3173 pbw polyisobutylene (PIB) (Mn 1890) and 198 pbw of maleic anhydride (MALA), yielding a molar ratio of maleic anhydride to polyisobutylene of 1.2, was heated from 135 to 195°C while chlorine (131 pbw, molar ratio of chlorine to polyisobutylene of 1.1) was introduced into the mixture over five hours. The mixture was then heated to 200°C for another two hours. The excess maleic anhydride was removed by evaporation under reduced pressure yielding a product with acid value of 0.84 mmol/g and active matter of 73% m/m, corresponding to a molar equivalent ratio of succinic anhydride

groups per equivalent polyisobutenyl group (SUC/PIB) of 1.15.

B) <u>Preparation of polyamide derivatives (succinimides)</u>

The PIB-succinic anhydride product of A) was diluted to about 50% AM with mineral oil and reacted at 180°C with penta-ethylene hexamine (PEHA) at a succinic to amine ration of 2:1 for about 3 hours. The reaction mixture was then filtered to yield the desired product.

Additional products of this invention were prepared following procedures generally similar to the foregoing, but substituting PIB of molecular weight 2480 and, in one case, also substituting a higher ethylene polyamine (HEPA) for the PEHA.

C) <u>Engine Testing</u>

The products prepared according to the above procedures were each blended (as a concentrate in mineral oil and in an amount giving 4% wt of test product) with an SAE 10W/40 luboil containing some 12% w/w of of an additive package comprising an overbased salicylate detergent, a V.I. improver, a zinc-based anti-wear additive and a polymethacrylate pour point depressant. The resulting oil was then evaluated according to the sequence VE (as described in "Sequence VE test procedure", 7th draft dated 19th May, 1988; ASTM Monitoring Center, 4400 5th Avenue Pittsburgh USA).

For the purposes of comparison, similar evaluations were carried out on commercially available products SAP 220 and LZ 6418 which differ from those of the present invention in

having either a lower M_n PIB or a higher molar equivalent ratio than the invention products.

The results of those VE tests are set out in the Table below, together with the nature of relative proportions of the reactants from which each product derives. In this Table the amine reactant is identified as TETA (triethylene tetramine), TEPA (tetra-ethylene pentamine), PEHA (penta-ethylene hexamine) or HEPA (higher ethylene polyamine) and the engine test results are given under the following conventional codings:-

RAcS = Rocker Arm Cover Sludge
AES = Average Engine Sludge
PSV = Piston Skirt Varnish
AEV = Average Engine Varnish

For the sludge and varnish measurements the results are on a 0-10 rating where 10 = zero sludge or varnish.

TABLE

	PRODUCT				ENGINE TESTING			
Code	PIB Mn	PIB/MALA molar equiv-alent	Amine	Coupling Ratio	RACS	AES	PSV	AEV
1 (H)	1890	1.15	PEHA	2.0	9.20	9.30	6.54	6.15
2 (I)	2480	1.20	PEHA	2.5	8.16	9.02	7.13	5.73
3 (J)	2480	1.20	HEPA	2.5	8.19	9.04	6.95	6.15
Compar-ison A (LZ 6418)	c.1850	c.1.75	TEPA	c.2.0	8.14	8.93	7.13	5.76
Compar-ison B (SAP 220)	950	1.00	TETA	2.0	5.08	6.30	6.53	4.38

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Claims

1. Oil-soluble dispersant useful as luboil additive which comprises a polyolefin substituted dicarboxylic acid or anhydride, in which the number average molecular weight (Mn) of the polyolefin is from 1500 to 5000 and the molar equivalent ratio (as hereinbefore defined) of dicarboxylic acid groups to equivalent of polyolefin substituent is less than 1.3.
2. Dispersant as claimed in claim 1 wherein the polyolefin has a molecular weight (Mn) between 1800 and 3000.
3. Dispersant as claimed in claim 1 or 2 wherein the polyolefin is polyisobutylene.
4. Dispersant as claimed in claim 1,2 or 3 wherein the ratio of weight average and number average molecular weights (Mw/Mn) of the polyolefin is from 1.5 to 4.0.
5. Dispersant as claimed in claim 1,2,3, or 4 wherein the dicarboxylic acid is succinic acid.
6. Dispersant as claimed in any one of the preceding claims wherein the dicarboxylic acid/polyolefin molar equivalent ration is 1.0 to 1.2.
7. Dispersant as claimed in any one of the preceding claims wherein the polyolefin-

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substituted dicarboxylic acid or anhydride is further reacted with a C_{6-50} amine containing 4 to 10 nitrogen atoms and/or an alkane polyol containing at least two hydroxy groups.

8. Dispersant as claimed in claim 7 wherein the amine is a polyamine of formula

$$NH_2(CH_2)_n - [NH(CH_2)_n]_m-NH_2$$

wherein n is 2,3 or 4 and m is 2 to 8.

9. Dispersant as claimed in claim 8 wherein the polyamine is tetraethylene pentamine, penta ethylene hexamine or higher ethylene polyamines.

10. Dispersant as claimed in claim 8 or 9 wherein the molar coupling ratio of dicarboxylic acid to amine is between 1.5:1 and 3:1.

11. Dispersant as claimed in claim 7 wherein the polyol is pentaerythritol.

12. Dispersant as claim in claim 7 or 11 wherein the molar ratio of alcohol to dicarboxylic compound is between 0.6:1 and 1.3:1.

13. Dispersant as claimed in any of the preceding claims which has been subjected to a post-treatment as hereinbefore described.

14. Dispersant as claimed in claim 1 substantially as hereinbefore described.

15. Lubricating composition which comprises a major proportion of a lubricating oil and a minor proportion of a dispersant as claimed in any one of the preceding claims.

16. Lubricating composition as claimed in claim 15 which contains from 0.1 to 10%w, based on the total composition, of the dispersant as claimed in any one of the preceding claims.

17. Lubricating oil concentrate which comprises a lubricating oil and 10 to 80%w (based on the

total concentrate) of a dispersant as claimed in any one of the preceding claims.

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